

N°7

News

International Newsletter

December 2015

Editorial

The current issue of ICMPE-News focuses on our recent activities in the fields of antibacterial materials, selective chemistry, and energy. These works have been conducted in 2015 and sought to bring some answers to the societal challenges faced by our modern world, as recently highlighted at the COP 21 held in Paris in last December. More fundamental researches are still needed to bring ingenious solutions to our fast changing environment. As highlighted in page 4, we are honored to host skillful and distinguished PhDs, engineers and scientists eager to conduct new science and proud to participate to the dissemination of our activities.

Michel LATROCHE, Director of ICMPE.



Front cover of Review of Scientific Instrument. Eric Alleno and collaborators (ICMPE, ICCMO, CRISMAT, ICMCB, EMPA, ICG, CEA, IJL, ASCR) have been strongly involved in the statistical processing of the data of a multi-instrumental Round Robin Test to evaluate the uncertainty on the figure of merit of thermoelectric materials, a quantity required to evaluate their energetic efficiency. This will help better comparison of the measurements performed in laboratories across the world and provides guidelines for improving the instrument. *Rev. Sci. Instrum.* vol. 86, Issue 1.

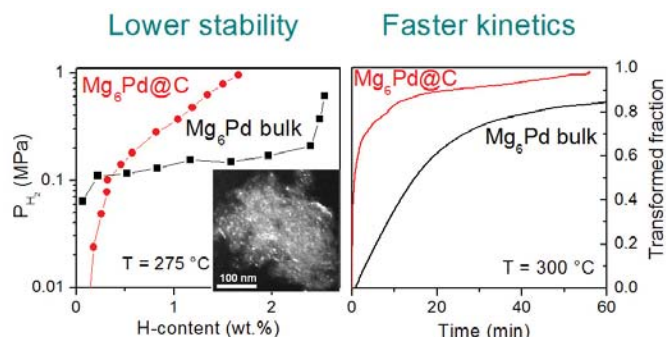
Energy Storage



Altering structural and hydrogenation properties of complex Mg₆Pd alloy by nanoconfinement

Mg₆Pd compound is a particular complex metallic alloy. It crystallizes in a large cubic structure with lattice parameter ~ 2 nm and is able to store significant amount of hydrogen (4.5 wt.%). However, hydrogen recovery requires heating above 300 °C and is characterized by sluggish reaction kinetics as result of formation of MgH₂ and Mg-Pd intermetallics leading to long range mass transport of metallic species. We here experimentally demonstrate that both structural and hydrogenation properties of Mg₆Pd can be strongly altered by nanoconfinement in porous carbon.

Mg₆Pd@C nanoparticles as small as 4 nm have been synthesized inside the cavities of a porous carbon by an original two step infiltration/impregnation of Mg and Pd. Structural studies by X-ray absorption spectroscopy reveal a simpler atomic arrangement in Mg₆Pd@C nanoparticles than in bulk when the nanoparticle size approaches the unit-cell dimensions. As for hydrogen storage properties, both thermodynamic and kinetic properties also differ for Mg₆Pd@C nanoparticles as compared to the bulk alloy. The hydrogenation kinetics of the Mg₆Pd@C nanoparticles are significantly faster than bulk and are stable for at least 10 sorption cycles. Thermodynamic destabilization of the hydrided state is also observed for the nanoconfined particles.



M. Ponthieu, Y. S. Au, K. Provost, C. Zlotea, E. Leroy, J.F. Fernández, M. Latroche, P.E. de Jongh and F. Cuevas, *J. Mater. Chem. A*, 2014, 2, 18444.

Contact : cuevas@icmpe.cnrs.fr



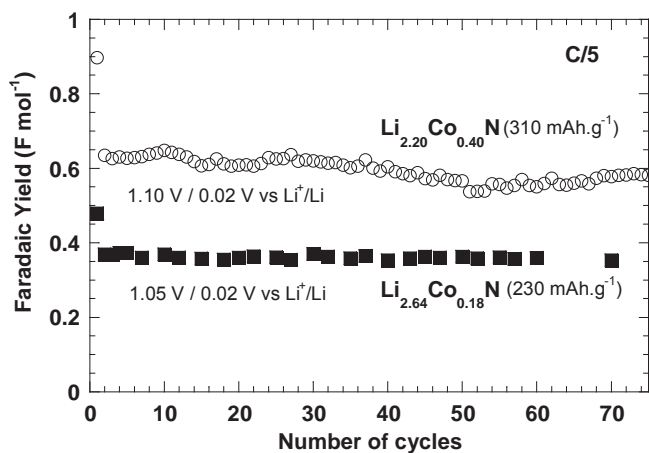
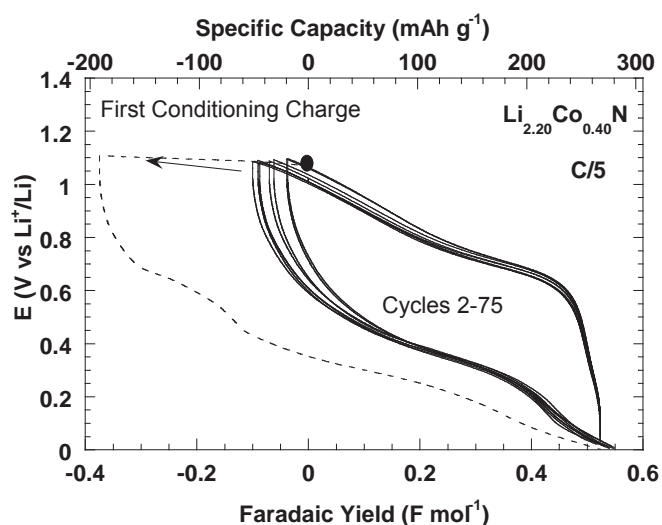
UNIVERSITÉ
PARIS-EST CRÉTEIL
VA. DE MARNE

Energy Storage

Optimization of cycling properties of the layered lithium cobalt nitride $\text{Li}_{2.20}\text{Co}_{0.40}\text{N}$ as negative electrode material for Li-ion batteries

An optimization of the specific capacity exhibited by the best layered lithiated cobalt nitride $\text{Li}_{2.20}\text{Co}_{0.40}\text{N}$ is proposed by using a conditioning electrochemical oxidation up to 1.1V before cycling in the 1.1V-0.02V range. This initial charge process allows the $\text{Co}^{3+}/\text{Co}^{2+}$ redox couple to be involved in the cycling process in addition to the $\text{Co}^{2+}/\text{Co}^+$ couple as in the 1V-0.02V voltage range. A new electrochemical fingerprint is obtained with a single step at 0.4/0.8V for the discharge-charge process and a specific capacity of 310 mAh g^{-1} at C/5 which constitutes a huge improvement compared to 130 mAh g^{-1} recovered in the conventional 1V-0.02V potential window. This high capacity value and the excellent capacity retention of 100% over at least 75 cycles make $\text{Li}_{2.20}\text{Co}_{0.40}\text{N}$ a promising anode material for Li-ion batteries.

$\text{Li}_{2.20}\text{Co}_{0.40}\text{N}$ constitutes the best metallic nitride with Li_7MnN_4 both working according to an insertion reaction mechanism. In situ XRD investigations are under progress to describe in detail the Li insertion-extraction process in this layered host lattice characterized by the existence of a large amount of lithium vacancies.



J. B. Ducros, S. Bach, J. P. Pereira-Ramos, P. Willmann, *Electrochim. Acta*, 167 (2015) 20

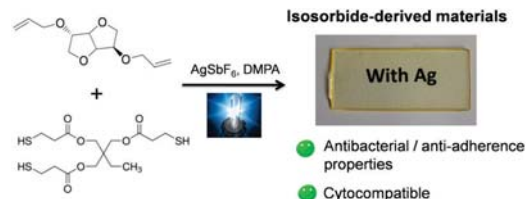
Contact : pereira@icmpe.cnrs.fr

Antibacterial materials

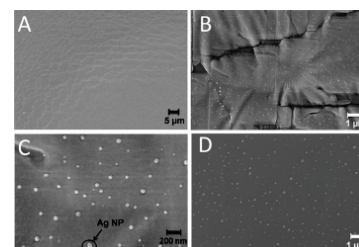
Photoinduced Development of Antibacterial Materials Derived from Isosorbide Moiety

Straightforward method for immobilizing *in situ* generated silver nanoparticles on the surface of a photoactivable isosorbide-derived monomer is developed to design a functional material having antibacterial properties. The photoinduced thiol-ene mechanism involved is described by the electron spin resonance/spin trapping technique. The resulting materials with or without silver nanoparticles (Ag NPs) were used as films or as coatings on glass substrate. The photoinduced Ag NPs, which are *in situ* generated upon light irradiation according to a fast photoreduction process, were randomly and homogeneously distributed on the surface and within the composite films. The resulting material including silver nanoparticles led to a reduction by 98% of the adherence of *S. aureus* and *E. coli* after 6 h of incubation without significantly affecting the adhesion and proliferation of NIH 3T3 fibroblastic cells. Finally, these isosorbide-derived materials could be also used as coatings according to their rubberlike state and are thus adapted to coat compliant substrates such as elastomers used in the fabrication of catheters (silicons, polyurethane), textiles, or hand-care utensils like pliers.

Elaboration of antibacterial materials based on isosorbide derivatives



SEM images : surface of photo-induced films containing (A) DIALI/Trithiol/DMPA ; (B, C) DIALI/Trithiol/DMPA/AgSbF6 ; (D) cross section of the photo-induced films containing Ag nanoparticles



C. Lorenzini, A. Haider, K. Inn-Kyu, M. Sangermano, S. Abbad-Andaloussi, P.E. Mazeran, J. Lalevee, E. Renard, V. Langlois, D.L. Versace, *Biomacromolecules* 16 (2015) 683-694

Contact : versace@icmpe.cnrs.fr

Past workshops

- The workshop "Nanotech-Nanotox of Soft Nanosystems", conducted within the Marie Curie Network ITN NANOS3 "Soft Small and Smart: Design, Assembly, Dynamics of Novel Nanoparticles for Industrial Applications" was held on May 20-21 2015 at ICMPE (C. Amiel).



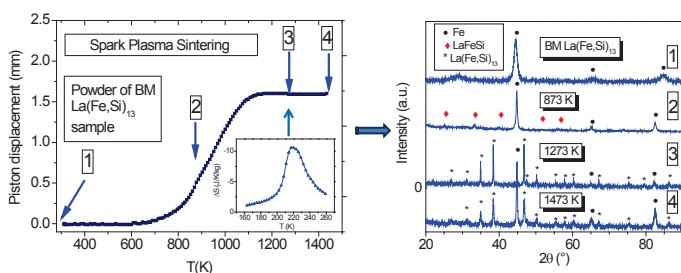
- Two workshops were organized (Fédération Française de Recherche sur les Matériaux) on October 8 and 9 2015. «le Fe des alliages entropie» on November 10-11 2015 are planned in 2016.



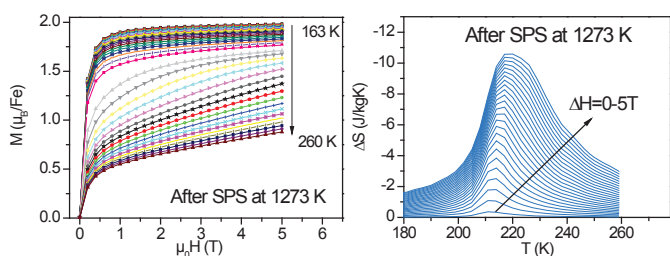
Fast Synthesis of Magnetocaloric Compound by SPS

Magnetization-demagnetization cycles near a magnetic transition induce a magnetocaloric effect (MCE) which can be used to produce energy friendly heat pump by avoiding the greenhouse refrigerant gas present in conventional systems. Magnetic heat pumps are also more efficient, more compact and less noisy. Development of efficient magnetocaloric materials is therefore a challenge for such application. Giant MCE has been discovered in $\text{La}(\text{Fe,Si})_{13}$ type compounds. Their Curie temperature can be adapted either by Fe substitution or light element insertion. However, alloy synthesis requires several days of heat treatment to obtain the efficient NaZn_{13} type phase. We have shown that this phase can be obtained by high energy ball milling (BM) of LaSi , Fe and Si followed by heat treatment of only 30 min at 1393 K.

The magnetic devices require also shaping the material in thin plates or small spheres to obtain efficient heat transfer. In this paper, we demonstrate that it is possible to synthesize and sinter in only one step $\text{La}(\text{Fe,Si})_{13}$ disks by Spark Plasma Sintering (SPS). BM powder is introduced into graphite dies and forms the NaZn_{13} phase at 1273 K under a pressure of 50 MPa.



Piston displacement and X ray diffraction patterns



Magnetic curves and corresponding magnetic entropy variation

A. Patissier and V. Paul-Boncour, *J. Alloys Compds*, 2015, 645, 143-150

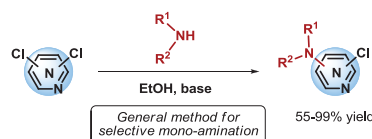
Contact : paulbon@icmpe.cnrs.fr



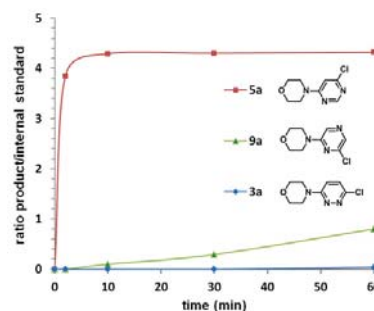
Selective mono-amination of dichlorodiazines

Diazine rings such as pyridazines, pyrimidines, and pyrazines are privileged scaffolds in medicinal chemistry as many of their substituted derivatives exhibit a wide range of biological activities. They have also found several types of applications in agrochemistry, material science and in supramolecular chemistry. As a result, although a considerable amount of work has been described in the literature on the preparation and characterization of these molecular systems, no general methods have ever been proposed for the amination of related dichlorodiazines via nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) methods.

In this article, we describe the first general study on the reactivity of dichlorodiazines towards primary and secondary amines (including heterocyclic and heteroaromatic rings). Assessment of the reaction parameters (solvent, temperature, base, amount of the amine etc.) provided two separate sets of conditions for the selective mono-amination on four key types of dichlorodiazines (i.e. 3,6-dichloropyridazine, 4,6- and 2,4-dichloropyrimidines, and 2,6-dichloropyrazine).



Moreover, in order to establish a reactivity scale of dichlorodiazines toward amines, an equimolar mixture of 3,6-dichloropyridazine, 4,6-dichloropyrimidine and 2,6-dichloropyrazine was allowed to react with morpholine in ethanol at 40°C in the presence of a base (NEt_3). Monitoring of the reaction products formation clearly shows that 4,6-dichloropyrimidine is far more reactive than 2,6-dichloropyrazine and 3,6-dichloropyridazine in the $\text{S}_{\text{N}}\text{Ar}$ reaction with amines. Indeed, 4,6-dichloropyrimidine reacts instantly with morpholine, followed by 2,6-dichloropyrazine, whereas 3,6-dichloropyridazine is almost unreactive at 40°C.



S. Sengmany, J. Lebre, E. Le Gall, E. Léonel. *Tetrahedron*, 2015, 71, 4859-4867.

Contact: sengmany@icmpe.cnrs.fr



workshops were organized by FERMI (Fédération pour l'Enseignement et la Recherche en Mécatronique et la Métallurgie en Île-de-France - Un Métal Incontournable!) (50 participants) and «Autour des matériaux multicomposants de haute performance» (May 11. Two other workshops were held in 2016.

• On December 2-3, AFICEP (P. Dabo) and Elastopôle (B. Martin), in collaboration with ICMPE (E. Léonel), have held a technical workshop on the functionalization of elastomers and polymers by surface treatments. Academic, technical centers and industrial partners have presented the latest evolutions in the field.

ICMPE hosted the 6th workshop "Batteries Lithium en Île-de-France" organized by J.-P. Pereira-Ramos (ICMPE) and H. Groult (PECSA), the 15th of December 2015. The latest results on Li and Na ion batteries have been presented during this meeting.

Contact: pereira-ramos@icmpe.cnrs.fr

Distinctions

Loïc Perrière, research engineer at ICMPE-MCMC and in charge of our metallurgical materials elaboration platform, received the **Jean Rist Medal** from the SF2M in 2015. This medal is awarded as an encouragement to young metallurgists and materials scientists in view of their remarkable scientific achievements.



During the meeting of the GDR HySPàC held the 14-16th October 2015 in Porticcio, Corsica, **Véronique Charbonnier**, a PhD student at ICMPE, was awarded the prize of best oral presentation for the STOPHE axis (Storage, Production and Purification of Hydrogen). Her presentation focused on "optimizing the composition of Y₂Ni₇ system for application in the field of Ni-MH".



Congratulations to **Carine Mangeon**, **Tina Modjinou** and **Seydina Kebe** who got the 1st prize for Communication and the 2nd and 3rd Innovation Award in the Doctoriales organized by the University of Paris-Est, the 4-9th of October 2015 in Chamarande. Felicitations also to **Asma Bensghaïer** who received an award at the 6th European Conference on Applications of surface and interface analysis in Granada, Spain (28/9-1/9/2015).



Welcoming our new researchers

Marc Presset has joined the **ESO Team of ICMPE** as Assistant Professor of the Faculty of Science at UPEC since the 1st of September 2015. He will work on multicomponent reactions with Pr. Le Gall.



ICMPE acknowledges the contribution of several of its members in the writing of reviews, books and book chapters

Dyes and Chromophores in Polymer Science, 2015 John Wiley & Sons, Ed. J. Lalevee and J.-P. Fouassier, with **Chapter 10: Photosynthesized High-Performance Biomaterials** (pp. 327-359) by Julien Babinot, Estelle Renard, Valérie Langlois and Davy-Louis Versace.

Comprehensive Guide for Mesoporous Materials, 2015 Nova Science Publishers, Ed. M. Aliofkhaezai, with **Chapter 7 "Engineering nanoporous polymeric materials from nanostructured macromolecular frameworks"** (pp. 159-184) by D. Grande and B. Le Droumaguet.

Surface Modification of Biopolymers, 2015 John Wiley & Sons, Ed. V. K. Thakur, A. S. Singha, with **Chapter 6: Tailoring Surface Properties of Degradable Poly(3-Hydroxyalkanoates) for Biological Applications** (pp. 150-173) by Estelle Renard, Davy-Louis Versace, Julien Babinot and Valerie Langlois.

Highlights

Valérie Langlois (ICMPE-SPC) participated in the show Docu-Debate on Public Sénat, broadcast after the documentary "Plastics, when our waste worth gold" (6th of June 2015). The composition of the board was: K. Mourjane, M. Rivasi (European deputy, Europe Ecologie Les Verts), É. Brac de la Perrière, CEO of Eco-Emballages. Available on the website <http://publicsenat.fr>.

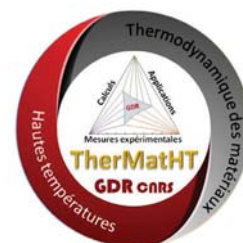


A new Master formation in material science and engineering, **Matériaux Avancés et Nanomatériaux (MAN)**, has been created this year by UPEC, UPEM and Ecole Nationale des Ponts et Chaussées (ENPC). Lecturers and researchers at ICMPE are strongly involved in this new formation, as well as in the already existing Masters: **Polymères fonctionnels** and **Chimie des Molécules Bioactives**.



The goal of **MAN** is to train students in the field of functional materials for industry and research sectors such as: elaboration of metals, alloys or inorganic materials; production, storage and conversion of energy; aerospace industry; remediation of industrial wastes. It aims to develop skills in synthesis and implementation of high-tech materials as well as in materials characterization and modeling.

J.-M. Joubert, J.-C. Crivello (ICMPE-CMTR) were involved in the organization and teaching of the summer school "*La donnée thermodynamique : de l'acquisition à l'application*". This school is linked to the GdR TherMatHT (Thermodynamique des Matériaux à Haute Température). It has taken place in September 13-18, 2015 at the CNRS Center of Oléron with 50 participants. <http://gdr-thermatht.cnrs.fr/>.



ICMPE News

Publisher : Michel Latroche - Coordination : Stéphane Bastide

→ To subscribe, contact: newsletter@icmpe.cnrs.fr

ICMPE
2-8, rue Henri Dunant
94320 Thiais - FRANCE
Tel: +33 (0)1 49 78 11 81
Fax: +33 (0)1 49 78 11 66
<http://www.icmpe.cnrs.fr>

